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POSSIBILITY OF OBTAINING CERAMOGRAHITE USING QUARTZ – FELDSPAR RAW MATERIAL FROM UKRAINE

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The results of investigations on the use of quartz – feldspar rock from Ukraine (granites and pegmatites) as flux in the production of ceramic-stone articles are presented. A theoretical estimate is made of the fluxing capacity of rock, and justification is given for the need to use in the paste compositions additives that lower the viscosity of the melts. The effect of the type and amount of fluxes and additives on the water absorption, firing shrinkage, and their proneness to deform is investigated. The ranges of optimal paste compositions which give ceramic materials with the properties of ceramogranite are determined.

In the last few years, interest in ceramic-stone construction materials, especially facing materials with a host of properties that are important for practice applications, has increased substantially. Such materials include, first and foremost, ceramogranite — a relatively new type of ceramic tile whose production and use are growing most rapidly. The main properties of ceramogranite that are important in practice are its high mechanical strength, durability, and in consequence longevity; this is due to the low porosity of the articles and virtually zero water absorption (less than 0.5%). These properties together with the high quality of the design of articles, their architectural expressivity, and ecological safety make ceramogranite a desirable material in modern construction practice and make it possible to use it to make bold designs a reality.

Foreign manufacturers produce a substantial fraction of ceramogranite tiles for the domestic market. Enterprises manufacturing the construction material exist in the south-eastern and central parts of Ukraine. However, the capacity of the operating production lines is low. Since Ukrainian high quality ceramic raw material does exist, including for obtaining materials with a densely sintered structure, the problem of developing compositions for ceramic pastes producing ceramogranite, which can serve as a base for creating import-replacing technologies for this popular type of construction material, becomes relevant.

Analysis of sources of information concerning the typical compositions of ceramogranite pastes shows that over the entire period of the existence of this material (approximately

20 years) the compositions of the mixtures have undergone definite changes. This was done so that manufacturers could decrease energy consumption in production by switching to accelerated and rapid firing regimes at relatively low temperatures. The paste compositions change in the direction of higher contents of the refractory component (kaolin) and increasing the amount of plastic clays and natural fluxes. A comparative characteristic of the charge compositions of the pastes for obtaining ceramic tiles with different density shows that as the degree of sintering of the material increases, the fraction of fluxes increases correspondingly — from 10% for tile with 16% water absorption to 45 – 50% for tile with 0.5% water absorption [1]. Hence it follows that it is impossible to develop a technology for densely sintered ceramic materials obtained using accelerated and fast firing regimes without using initial components which act as energetic fluxes and provide the required level of sintering of the material over a short period of time.

Feldspars (natural mixtures of potassium, sodium, calcium, and barium aluminosilicates) have traditionally fulfilled the role of effective fluxes in the compositions of fine-ceramic pastes. Domestic deposits of conditioned feldspars are now practically exhausted. At the same time, quartz – feldspar rock of magmatic origin, where feldspars are the main rock-forming minerals, are widely disseminated in the massifs of the Ukrainian crystalline plate. This mineral composition makes it possible to consider such rocks as substitutes for feldspars in the technology for producing ceramic stone articles. Granites and pegmatites are the main quartz – feldspar rocks found in virtually unlimited quantities in Ukraine. As a result, they are of greatest interest to specialists.

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TABLE 1.

Initial material	Mass content, %							calcination loss
	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Fe ₂ O ₃	
Pegmatite	75.40	13.85	0.49	0.17	4.43	3.17	0.70	1.79
Granite	65.60	15.70	2.60	1.50	6.10	3.00	4.20	1.30

TABLE 2.

Initial material	Mass content, %			
	albite	orthoclase	anortite	quartz
Pegmatite	28	28	3	41
Granite	28	39	12	21

TABLE 3.

Indicator	Melt	
	pegmatite	granite
Liquidus temperature, °C	1140	1060
Logarithm of melt viscosity [Pa · sec]:		
at liquidus temperature	3.65	4.10
at 1200°C	3.35	3.36
Melt surface tension, N/m, at liquidus temperature	0.276	0.279

Granite is an intrusive holocrystalline rock characterized by medium- and fine-grain structure which usually consists of orthoclase, acidic plagioclase, and quartz. Magnesia-ferruginous compounds (hornblende, biotite, muscovite, and others) can be present in granites as accessory minerals. Pegmatites are characterized primarily by a similar mineral composition, but they are distinguished by a definite ratio of feldspars and free quartz (70–75% and 30–25%, respectively). Another characteristic feature of pegmatites, which is due to their semideep bedding in the Earth's crust, is the so-called pigmatoid structure characterized by coarse grains (sometimes even gigantic grains of individual mineral components) and regular intergrowth of quartz and feldspars [2].

This type of mineral composition of granites and pegmatites permits classifying these rocks according to their fluxing action in ceramic pastes as type-I fluxes — materials which form a liquid phase by melting themselves. The temperatures at which the main rock-forming minerals in granites and pegmatites — orthoclase, albite, anortite, quartz [3], and individual mineral mixtures [4] — melt are known. However, the natural qualitative and quantitative fluctuations of the quite complex mineral composition of rock from one deposit to another (especially for granites) caused by the different conditions under which magma congeals and the bed-

ding of the rock, observed in practice make it necessary to assess separately, each time, their fluxing and action in application to each specific initial material.

The goal of the present investigation is to study the meltability of quartz – feldspar rock from the central and southwestern parts of Ukraine —

granites from the Poltava region and pegmatites from the Zhitomir region — in order to use them as fluxes in fine-ceramic pastes for obtaining ceramogranite. A previously proposed method of physical – chemical prediction of the fluxing capacity of melts was used to determine the capability of granite and pegmatites to form melts at the temperatures used in ceramogranite technology [1].

The method is based on calculations performed in oxide silicate systems and systems of minerals, the results of which can be used to estimate theoretically the chemical composition and quantity of melt formed when the rock is heated and to calculate the main properties of the melt. The computational data obtained, taken as a whole, make it possible to determine the temperature conditions for applicability of melt and the effectiveness of its fluxing action with accuracy sufficient for practical purposes. The initial data for performing the calculations is the chemical composition of the initial material, according to which its mineral composition can be determined. The chemical and mineral compositions of the quartz – feldspar rocks studied are presented in Tables 1 and 2.

The liquidus temperature of the material was determined according to the mineral composition of the initial material studied, presented on a D. F. Scherer diagram. The most technologically important properties of the melt — viscosity and surface tension — were calculated according to its chemical composition (Table 3).

As one can see, granite possesses a lower liquidus temperature than pegmatite. Evidently, this is due to the characteristic features of the chemical – mineral composition of the rock (elevated content of free silica in pegmatite with a low content of plagioclases). At the same time, for a virtually identical surface tension of the melts of both rocks, the viscosity of the granite melt is characterized by higher values; this is explained by the predominance of orthoclase in the feldspar component of this rock. On the whole, the viscosity of both melts ($10^{3.35} - 10^{4.1}$ Pa · sec) falls outside requirements for this composition for rapid liquid-phase sintering of the ceramic ($10^2 - 10^3$ Pa · sec), which will decrease the fluxing action of the melts.

One way to decrease the viscosity of the liquid phase and therefore activate sintering is to introduce into the melt additives that change its structure and increase mobility [5]. Materials containing oxides of alkaline-earth metals can serve as such additives for alkali-containing aluminosilicate melts of the quartz feldspar initial material considered here. The mechanism of their action consists in destroying the structure

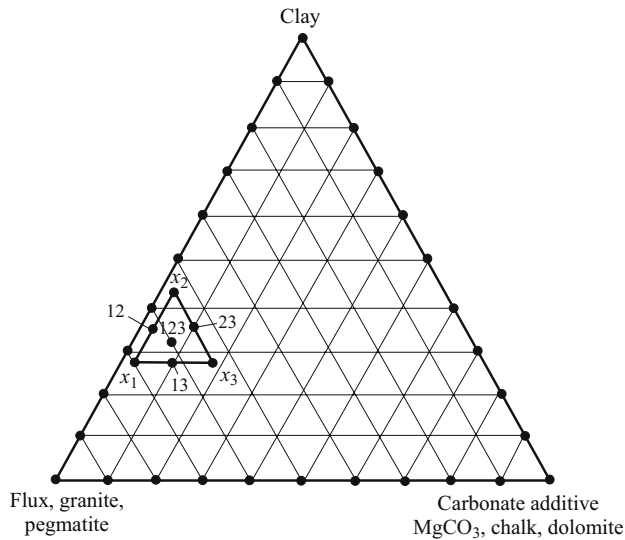


Fig. 1. Simplex – lattice planning of an experiment: x_1) 70% flux, 28% clay, and 2% carbonate additive; x_2) 55% flux, 43% clay, and 2% carbonate additive; x_3) 55% flux, 28% clay, and 17% carbonate additive.

of the anionic complexes of $\text{Si}_x\text{Al}_y\text{O}_z$ melts as a result of cations with a low binding energy with oxygen penetrating into them, fragmentation of the complexes, and increasing their mobility, which as a whole decreases the viscosity of the melt and improves the sinterability of the paste. We used chalk CaCO_3 , magnesium carbonate $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, and dolomite $\text{CaMg}(\text{CO}_3)_2$ as additives containing alkaline-earth oxides and activating sintering.

The method of simplex – lattice planning of experiments using Scheffe plans was used to develop the batch compositions of ceramogranite pastes in order to study the effect of the type and quantity of quartz – feldspar rock and additives on the sinterability of pastes. Refractory clay from the firm Vesko (Druzhkovka in Donetsk Oblast') was used as the binding component in the ceramic pastes. The investigations were performed in an elementary concentration triangle flux – clay – carbonate additive, each point of which consisted of a three-component composition of raw materials. The plan of the experiment and the working intervals of the content of the components in the batch mixtures are presented in Fig. 1.

These samples were prepared by semidry pressing of powders with moisture content 8 – 9%, consisting of initial materials prepared beforehand. The quartz – feldspar rock was ground to a thickness permitting passage through a No. 0063 sieve with 3 – 5% residue. The samples were sintered in a laboratory muffle furnace at 1000 and 1100°C with holding time 1 h at the final temperature. Subsequently, the water absorption and firing shrinkage were studied for the materials obtained at different temperatures based on the initial mixtures of two types (pegmatite and granite-containing). After the experimental data were analyzed statistically and the incomplete third-order polynomials were checked for

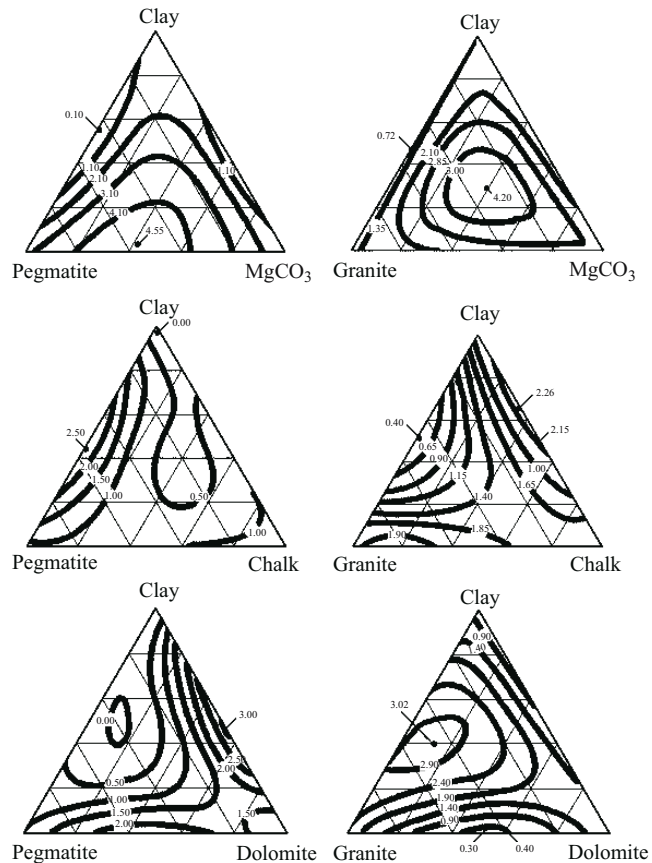


Fig. 2. Diagrams of batch compositions – water absorption for materials obtained using pegmatite and granite at 1100°C.

adequacy for each type of material, isolines of different values of the indicated properties were obtained.

The sinterability of pegmatite and granite-containing compositions was assessed first according to the water absorption of these samples as the main characteristic of ceramogranite tiles which should not exceed 0.5% (EN 14411 ISO 105445). The effect of the batch composition of the pastes on the water absorption of these samples (%), which were obtained at 1100°C, is illustrated in the diagrams presented in Fig. 2. It should be noted that similar data for samples obtained at 1000°C are not presented, since the required degree of densification of the materials (water absorption $\geq 10\%$) is not achieved at any temperature, despite the sinterability of the pastes.

Analyzing the data in Fig. 2 on the sintering action of pegmatite and granite shows that both rocks are effective fluxes — using these rocks in the quantity studied permits obtaining densely sintered materials with water absorption characteristics for ceramogranite. A comparative analysis of the sintering action of the carbonate additives showed that for pegmatite and granite-containing compositions samples obtained from pastes with MgCO_3 additive are characterized by the lowest degree of densification (maximum water content 4.20 and 4.55%, respectively). At the same time, it is

possible to obtain from the same pastes with correctly chosen batch composition samples with low water content also (0.10 – 0.72%), but in a very narrow range of batch compositions. The positive influence of chalk and dolomite on the sinterability of the pastes is virtually identical. Samples with water absorption in the range 0.4 – 3.0% were prepared from granite-containing pastes and samples with water absorption 0 – 3% were obtained from pegmatite pastes.

In studying the effect of the batch composition of the pastes on the volume firing shrinkage of samples, it was established that the largest shrinkage (32%) occurred for materials obtained from both types of pastes with MgCO_3 additive. Keeping in mind the known mechanism of liquid-phase sintering of ceramic, in accordance with which the surface tension of the melt plays the main role in the process of convergence of solid-phase particles, this effect of MgCO_3 can be explained precisely by enhanced surface tension of the melt with its participation. For example, according to the data in [6] the partial contribution of MgO_3 to the surface tension of the melt is 605.7, and the contribution for CaO is 540.

Analyzing the external appearance of the samples, it was found that when CaCO_3 is used in pastes in amounts ranging from 7.5 to 17.0% they deform at high temperature. This effect of calcium carbonate, in contrast to, for example, MgCO_3 , can be explained by its influence on the viscosity of the liquid phase. It is well-known that CaO lowers melt viscosity more effectively than MgO (the partial factor is 0.69 for CaO and 4.59 for MgO) [7]. In addition, as is well known, melts with participation of CaO are characterized by more rapid decrease of the viscosity with increasing temperature as compared with melts containing MgO . It should also be noted that the samples obtained using CaCO_3 but containing different fluxes (granite or pegmatite) also have a different degree of deformation — granite-containing pastes are more prone to lose their shape during sintering. This difference is explained by the properties of the flux melts. For example, according to the computational results presented in Table 3, at 1100°C (liquidus temperature 1060°C) pegmatite does not completely transform into melt.

The effect of $\text{CaMg}(\text{CO}_3)_2$ as a sintering activator is similar to that of CaCO_3 with respect to water absorption and firing shrinkage, but the proneness of samples to undergo deformation at high temperatures is expressed to a lower degree, especially in pegmatite pastes. This is explained by the fact that during sintering dolomite can form CaO and MgO . The latter oxide counters the effect of CaO as a component which effectively lowers the viscosity of the melt arising.

On the whole, comparing the properties of the samples obtained from pegmatite and granite-containing pastes with different carbonate additives, it should be noted that there exists for each mixture an optimal range of batch compositions which can be used to obtain materials with virtually zero water absorption, low firing shrinkage, and no tendency to deform at high temperatures. Exceptions are ceramic pastes with MgCO_3 additive, which cannot be recommended because of their substantial firing shrinkage (on the average 25%). For all granite-containing pastes and pegmatite pastes with dolomite as the additive, the optimal compositions are bound by the minimum content of carbonates (2%) with different ratios of flux and clay within the limits of the experimental interval of their content. Pegmatite ceramic pastes with $\text{Ca}(\text{CO}_3)_2$ are most promising and practicable; the range of optimal batch compositions is greatest for these pastes.

The theoretical and experimental investigations performed in this work have shown that Ukrainian quartz – feldspar rock can be used as substitutes for imported feldspars for producing ceramogranite tiles. The additional use of carbonate additives in the form of chalk and dolomite, which activate liquid-phase sintering, in the pastes makes it possible to obtain artificial material, characterized by the properties of natural stone, over a short period of time (1 h) and at relatively low temperatures (1100°C).

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